Spontaneously Twisted Nonchiral Nematic Liquid Crystals

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Nematic liquid crystals exhibiting a negative K_2 elastic constant are discussed on the basis of a microscopic model potential. Stability conditions are satisfied by taking into account higher order terms in the expansion of the free energy. A continuous Freederiks effect is predicted for systems with negative K_2.

1. Introduction

Miroscopic theories of nematic liquid crystals allow us to calculate from a few molecular parameters a number of macroscopic and static properties, such as the equation of state, the short and long-range order parameters and the visco-elastic coefficients. An attempt to provide such a microscopic theory which, for the more common nematics, fits the experimental data for the elastic constants and the long-range order parameters simultaneously, was introduced in [1]. From this theory it is possible to derive the microscopic potential which leads to a negative elastic constant K_2. The equilibrium state of the system described by such a potential would exhibit a spontaneously broken symmetry of the twist-type. Experimental evidence of this property can be obtained by the investigation of the Freederiks effect. Due to the negative value of K_2, a Freederiks effect would occur even for an arbitrary weak magnetic field. The purpose of this paper is to investigate this phenomenon from the microscopic point of view.

All the results have been obtained by the constant curvature approximation (CCA) derived from the mean-field theory; therefore this technique is described in Chapter 2. In order to test the CCA, we derived in Chapter 3 the formulas for the elastic constants K_1, K_2, and K_3. As K_2 can be negative, contrary to K_1 and K_3, we have to consider higher order terms in the free energy expansion for the twist deformation. Expansion coefficients occurring in the higher order terms are calculated by use of the CCA in Chapter 4. The stability conditions, numerical results and summary are presented in Chapter 5.

2. Constant Curvature Approximation (CCA)

Let us consider a nematic liquid crystal in a weak-ordering field, which varies slowly in space, so that the $\boldsymbol{m}(\boldsymbol{r})$ preferred orientation aligns everywhere along that field. Using Fig. 1 we can derive expressions for the field configuration corresponding to splay, twist and bend.

The derivation of the formula for splay, is as follows: Let the $\boldsymbol{m}$ director be situated along the directions of the lines of the bundle going out from the point of origin of the coordinate system. From simple algebra for the bundle of the lines we can obtain expressions for the unit vector which are parallel to these directions. These unit vectors will be our field configuration for splay. By analogy one can get expressions for bend and twist. The parameters which characterize these configurations are the constant curvatures: $\varepsilon_1 = 1/L_1$, $\varepsilon_2 = 1/L_2$, $\varepsilon_3 = 1/L_3$, where L_1 and L_3 are the distances between the point of origin (0, 0, 0) of the coordinate system and the centers of the samples, and L_2 is the spiral jump. Expressions for the $\boldsymbol{m}_i(\boldsymbol{r})$ vectors are the following:

$$\text{splay:}\quad \boldsymbol{m}(\boldsymbol{r}) = (x, y+L_1, 0)/\sqrt{(x+L_1)^2 + x^2}, \qquad (2.1\text{ a})$$

$$\text{bend:}\quad \boldsymbol{m}(\boldsymbol{r}) = (-(y+L_2), x, 0)/\sqrt{(y+L_3)^2 + x^2}, \qquad (2.1\text{ b})$$

$$\text{twist:}\quad \boldsymbol{m}(\boldsymbol{r}) = (\sin\phi(z), \cos\phi(z), 0), \quad \phi(z) = \pi z/L_2. \qquad (2.1\text{ c})$$

Since L_1, L_2 and L_3 are large (the director varies very slowly) we can treat ε_1, ε_2 and ε_3 as small parameters

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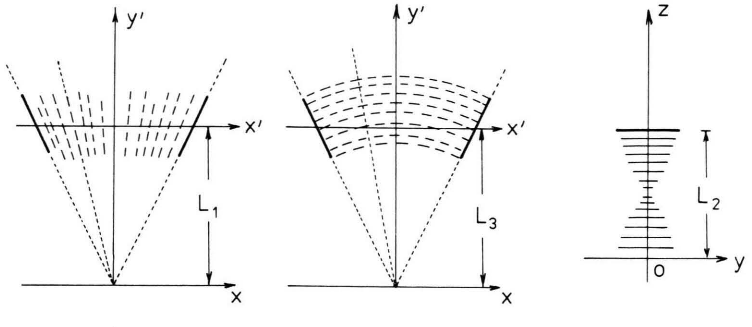

splay bend twist

Fig. 1. Field configurations for splay, bend, and twist.

of curvature. Therefore it is possible to expand $\boldsymbol{m}(\boldsymbol{r})$ into a power series with respect to ε:

$$\boldsymbol{m}(\boldsymbol{r}) = \boldsymbol{m}_0(\boldsymbol{r}) + \varepsilon\, \boldsymbol{m}_1(\boldsymbol{r}) + \varepsilon^2\, \boldsymbol{m}_2(\boldsymbol{r}) + \ldots . \tag{2.2}$$

The expansion coefficients due to splay, bend and twist have the following forms:

$$\begin{aligned}\text{splay:}\quad & \boldsymbol{m}_0 = (0, 1, 0), \quad \boldsymbol{m}_1 = (x, 0, 0),\\ & \boldsymbol{m}_2 = (-x\,y,\ -x^2/2,\ 0),\\ & \boldsymbol{m}_3 = (x\,y^2 - x^3/2,\ y\,x^2,\ 0);\end{aligned} \tag{2.3 a}$$

$$\begin{aligned}\text{bend:}\quad & \boldsymbol{m}_0 = (-1, 0, 0), \quad \boldsymbol{m}_1 = (0, x, 0),\\ & \boldsymbol{m}_2 = (x^2/2,\ -x\,y,\ 0),\\ & \boldsymbol{m}_3 = (-y\,x^2,\ x\,y^2 - x^3/2,\ 0);\end{aligned} \tag{2.3 b}$$

$$\begin{aligned}\text{twist:}\quad & \boldsymbol{m}_0 = (0, 1, 0), \quad \boldsymbol{m}_1 = (z, 0, 0),\\ & \boldsymbol{m}_2 = (0,\ -z^2/2,\ 0), \quad \boldsymbol{m}_3 = (z^3/6, 0, 0).\end{aligned} \tag{2.3 c}$$

Expansions of $\boldsymbol{m}(\boldsymbol{r})$ with respect to the constant curvatures will be the approximations of the local preferred orientations. We can apply them in the Frank energy of deformation [2]:

$$F_{\mathrm{d}} = \tfrac{1}{2}\int \mathrm{d}^3 r\,[K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2]. \tag{2.4}$$

Simple calculations show that the Frank energy of deformation expanded up to ε^2 is

$$F_{\mathrm{d}} = \tfrac{1}{2}(K_1\,\varepsilon_1^2 + K_2\,\varepsilon_2^2 + K_3\,\varepsilon_3^2)\cdot V + O(\varepsilon^4). \tag{2.5}$$

3. Testing of the CCA

In order to test the validity of the CCA we will derive the microscopic formulas for the Frank elastic constants. The starting point of this derivation is the comparison of two different forms of F_{d}, where only one of them includes elastic constants. The first form is the above mentioned Frank energy of deformation:

$$F_{\mathrm{d}} = \tfrac{1}{2}\int \mathrm{d}^3 r\,[K_{11}(\nabla\cdot\boldsymbol{n})^2 + K_{22}(\boldsymbol{n}\cdot\nabla\times\boldsymbol{n})^2 + K_{33}(\boldsymbol{n}\times\nabla\times\boldsymbol{n})^2]. \tag{3.1}$$

The second form reads [3]:

$$\beta F = -\tfrac{1}{2}\int f_{12}\,\tilde{\varrho}(\boldsymbol{n}_1\cdot\boldsymbol{m}(\boldsymbol{r}_1)) \cdot [\tilde{\varrho}(\boldsymbol{n}_2\cdot\boldsymbol{m}(\boldsymbol{r}_2)) - \tilde{\varrho}(\boldsymbol{n}_2\cdot\boldsymbol{m}(\boldsymbol{r}_1))]\,\mathrm{d}(1)\,\mathrm{d}(2), \tag{3.2}$$

where $\tilde{\varrho}(\boldsymbol{n}\cdot\boldsymbol{m}(\boldsymbol{r}))$ is the relative probability of a molecule at $\boldsymbol{r}$ having the orientation $\boldsymbol{n}$ (single particle distribution function), $\boldsymbol{m}(\boldsymbol{r})$ is the local preferred orientation and f_{12} the Mayer function $f_{12} = e^{-\beta U_{12}} - 1$.

Now we will apply the CCA to the avaluation of the forms (3.1) and (3.2) for F_{d} and βF.

The expansion of the single particle distribution function with respect to ε reads

$$\tilde{\varrho}(\boldsymbol{n}\cdot\boldsymbol{m}(\boldsymbol{r})) = \tilde{\varrho}(\boldsymbol{n}\cdot\boldsymbol{m}(\boldsymbol{r}))|_0 + \left.\frac{\mathrm{d}\tilde{\varrho}}{\mathrm{d}\varepsilon}\right|_0 \varepsilon + \left.\frac{\mathrm{d}^2\tilde{\varrho}}{\mathrm{d}\varepsilon^2}\right|_0 \frac{\varepsilon^2}{2!} + \ldots, \tag{3.3}$$

$$\tilde{\varrho}(\boldsymbol{n}\cdot\boldsymbol{m}(\boldsymbol{r})) = \varrho_0(\boldsymbol{n}\cdot\boldsymbol{m}_0) + \varrho_0'(\boldsymbol{n}\cdot\boldsymbol{m}_0)\,\boldsymbol{n}\cdot\boldsymbol{m}_1\,\varepsilon + \tfrac{1}{2}[\varrho_0''(\boldsymbol{n}\cdot\boldsymbol{m}_0)(\boldsymbol{n}\cdot\boldsymbol{m}_1)^2 + 2\varrho_0'(\boldsymbol{n}\cdot\boldsymbol{m}_0)\,\boldsymbol{n}\cdot\boldsymbol{m}_2]\,\varepsilon^2 + \ldots, \tag{3.4}$$

where ϱ_0 is the distribution function for the undistorted system and $\boldsymbol{m}_0$ the director of the undistorted system independent of the spatial coordinates.

Substituting (3.4) into (3.2) we obtain

$$\beta F = -\frac{\varepsilon^2}{2}\int f_{12}\,\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\,\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,\boldsymbol{n}_1\cdot\boldsymbol{m}_1(\boldsymbol{r}_1)\,\boldsymbol{n}_2 \cdot [\boldsymbol{m}_1(\boldsymbol{r}_2) - \boldsymbol{m}_1(\boldsymbol{r}_1)]\,\mathrm{d}(1)\,\mathrm{d}(2). \tag{3.5}$$

The remaining parts of F vanish because they include integrals of the odd function or they contain the difference

$$\varrho(\boldsymbol{n}\cdot\boldsymbol{m}_0(\boldsymbol{r}_1))-\varrho_0(\boldsymbol{n}\cdot\boldsymbol{m}_0(\boldsymbol{r}_2))$$

which is equal to zero since $\boldsymbol{m}_0(\boldsymbol{r}_1)=\boldsymbol{m}_0(\boldsymbol{r}_2)=\text{const.}$

Taking into account the explicit forms for $\boldsymbol{m}_0$, $\boldsymbol{m}_1$ and $\boldsymbol{m}_2$ (2.3 a) in the case of splay we obtain

$$\beta F=\frac{\varepsilon^2}{4}\int f_{12}\,\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\cdot\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,n_{1x}\,n_{2x}(x_1-x_2)^2\,\mathrm{d}(1)\,\mathrm{d}(2). \tag{3.6}$$

By introducing new coordinates $\boldsymbol{u}=\boldsymbol{r}_1-\boldsymbol{r}_2$ and $\boldsymbol{v}=\frac{1}{2}(\boldsymbol{r}_1+\boldsymbol{r}_2)$ we derive

$$\beta F=\frac{\varepsilon^2}{4}\int f_{12}\,\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\cdot\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,n_{1x}\,n_{2x}\,u_x^2\,\mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{n}_1\,\mathrm{d}\boldsymbol{n}_2\cdot V \tag{3.7}$$

where $\int\mathrm{d}\boldsymbol{v}=V$ is the volume of the sample.

On the other hand, restricting (2.5) to the case of splay we get

$$F_\mathrm{d}=\tfrac{1}{2}K_1\,\varepsilon^2\,V+O(\varepsilon^4). \tag{3.8}$$

Comparison of (3.7) and (3.8) yields

$$K_1=\frac{kT}{2}\int f_{12}\,\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\cdot\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,n_{1x}\,n_{2x}\,u_x^2\,\mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{n}_1\,\mathrm{d}\boldsymbol{n}_2, \tag{3.9}$$

where $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$ are the orientations of the molecules and $\varrho_0(\cos\theta)$ is the single particle distribution function for the undistorted system.

Poniewierski and Stecki [4] have derived microscopic formulas for the Frank elastic constants. They have used a system of coordinates where the z-axis lies along the director of the undistorted system. In our case the vector $\boldsymbol{m}_0$ plays this role; for splay it has the form $\boldsymbol{m}_0=(0,1,0)$. This means that for splay the vector $\boldsymbol{m}_0$ lies along the y-axis.

By analogous calculations we are able to find formulas for K_2 and K_3:

$$K_3=\frac{kT}{2}\int f_{12}\,\varrho_0'(\cos\theta_1)\cdot\varrho_0'(\cos\theta_2)\,n_{1x}\,n_{2x}\,u_z^2\,\mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{n}_1\,\mathrm{d}\boldsymbol{n}_2, \tag{3.10}$$

$$K_2=\frac{kT}{2}\int f_{12}\,\varrho_0'(\cos\theta_1)\cdot\varrho_0'(\cos\theta_2)\,n_{1y}\,n_{2y}\,u_x^2\,\mathrm{d}\boldsymbol{u}\,\mathrm{d}\boldsymbol{n}_1\,\mathrm{d}\boldsymbol{n}_2. \tag{3.11}$$

It turns out that these expressions are exactly the same as in [4]. This proves that the method described above is quite good for our attempts. However, on the one hand the CCA significantly shortens the calculations, and on the other hand it makes it possible to investigate higher-order terms in F, something which has been quite impossible so far. In the following chapters it will turn out that this achievement actually has a useful application.

4. Derivation of the Free Energy up to ε^4

We are considering the simplest case, i.e. free boundary conditions.

The expansion of F for the twist deformation in the case of positive K_2 up to ε^2 has only one minimum for $\varepsilon=0$, which corresponds to an undistorted sample. When K_2 is negative, the free energy has no absolute minimum and the system should collapse. Therefore we have to consider higher order terms in the expansion of (3.2). Extending all calculations up to the ε^4 we can obtain the following high-order terms of F:

$$-\varepsilon^4\int f_{12}\,\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\left[\frac{1}{3!}\varrho_0'''(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)(\boldsymbol{n}_2\cdot\boldsymbol{m}_1(\boldsymbol{r}_2))^3+\varrho_0''(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,\boldsymbol{n}_2\cdot\boldsymbol{m}_2(\boldsymbol{r}_2)\,\boldsymbol{n}_2\cdot\boldsymbol{m}_1(\boldsymbol{r}_2)+\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,\boldsymbol{n}_2\cdot\boldsymbol{m}_3(\boldsymbol{r}_2)\right]\boldsymbol{n}_1\cdot[\boldsymbol{m}_1(\boldsymbol{r}_1)-\boldsymbol{m}_1(\boldsymbol{r}_2)]\,\mathrm{d}(1)\,\mathrm{d}(2), \tag{4.1 a}$$

$$-\frac{\varepsilon^4}{8}\int f_{12}[\varrho_0''(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)(\boldsymbol{n}_1\cdot\boldsymbol{m}_1(\boldsymbol{r}_1))^2+2\varrho_0'(\boldsymbol{n}_1\cdot\boldsymbol{m}_0)\,\boldsymbol{n}_1\cdot\boldsymbol{m}_2(\boldsymbol{r}_1)]\cdot[\varrho_0''(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,((\boldsymbol{n}_2\cdot\boldsymbol{m}_1(\boldsymbol{r}_2))^2-(\boldsymbol{n}_2\cdot\boldsymbol{m}_1(\boldsymbol{r}_1))^2)+2\varrho_0'(\boldsymbol{n}_2\cdot\boldsymbol{m}_0)\,(\boldsymbol{n}_2\cdot\boldsymbol{m}_2(\boldsymbol{r}_2)-\boldsymbol{n}_2\cdot\boldsymbol{m}_2(\boldsymbol{r}_1))]\,\mathrm{d}(1)\,\mathrm{d}(2). \tag{4.1 b}$$

Substituting the explicit forms of $\boldsymbol{m}$ (2.3c) for the twist into (4.1) we obtain

$$\begin{aligned}
&\varepsilon^4 \left[\tfrac{1}{12} \int f_{12}\, \varrho_0'(\cos\theta_1)\, \varrho_0'''(\cos\theta_2)\, n_{1y}\, n_{2y}^2 [u_x^4/4 + 3/5\, u_x^2 R^2]\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\mathbf{u}\, V\right.\\
&\quad - \tfrac{1}{4} \int f_{12}\, \varrho_0'(\cos\theta_1)\, \varrho_0''(\cos\theta_2)\, n_{1y}\, n_{2y}\, n_{2z} [u_x^4/4 + 3/5\, u_x^2 R^2]\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\boldsymbol{u}\, V\\
&\quad - \tfrac{1}{2} \int f_{12}\, \varrho_0'(\cos\theta_1)\, \varrho_0''(\cos\theta_2)\, n_{1z}\, n_{2y}^2\, u_x^2 R^2/5\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\boldsymbol{u}\, V\\
&\quad + \tfrac{1}{2} \int f_{12}\, \varrho_0'(\cos\theta_1)\, \varrho_0'(\cos\theta_2)\, n_{1y}\, n_{2y} [u_x^4/4 + 3/5\, u_x^2 R^2]\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\boldsymbol{u}\, V\\
&\quad + \tfrac{1}{4} \int f_{12}\, \varrho_0'(\cos\theta_1)\, \varrho_0'(\cos\theta_2)\, n_{1z}\, n_{2z}\, u_x^2 R^2/5\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\boldsymbol{u}\, V\\
&\quad \left. + \tfrac{1}{4} \int f_{12}\, \varrho_0''(\cos\theta_1)\, \varrho_0''(\cos\theta_2)\, n_{1y}^2\, n_{2y}^2\, u_x^2 R^2/5\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, \mathrm{d}\boldsymbol{u}\, V\right],
\end{aligned} \tag{4.2}$$

where R is a radius of the spherical sample.

These formulas are written in a coordinate system consistent with the system which was used in [4]. We can express the radial parts of the integrals (4.2) with $\mathrm{d}\boldsymbol{u} = u^2\, \mathrm{d}u\, \mathrm{d}\varDelta$ ($\varDelta$ is a unit vector pointing into the direction of the vector $\boldsymbol{u}$) by the B_i^* coefficients. We assume that $R = \infty$ is here meaningless for the values of our integrals, which makes the calculations simpler:

$$\int_0^\infty [\exp\{-\beta U_{12}(\sigma/u)\} - 1]\, u^6\, \mathrm{d}u = \sigma^7 B_6^*(T^*), \tag{4.3a}$$

$$\int_0^\infty [\exp\{-\beta U_{12}(\sigma/u)\} - 1]\, u^4\, \mathrm{d}u = \sigma^5 B_4^*(T^*), \tag{4.3b}$$

where $T^* = kT/\gamma$ is the reduced temperature.

Introducing the dimensionless function $f(x) = (4\pi/d)\, \varrho(x)$ we transform (4.2) into a sum of the following terms:

$$\frac{\varepsilon^4}{12}\, \sigma_0^7 B_6^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f'''(2) \cdot A^7\, n_{1y}\, n_{2y}^3\, \varDelta_x^4\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, V, \tag{4.4a}$$

$$\frac{\varepsilon^4}{80\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f'''(2) \cdot A^5\, n_{1y}\, n_{2y}\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4b}$$

$$-\frac{\varepsilon^4}{4}\, \sigma_0^7 B_6^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f''(2) \cdot A^7\, n_{1y}\, n_{2y}\, n_{2z}\, \varDelta_x^4\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, V, \tag{4.4c}$$

$$-\frac{\varepsilon^4}{40\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f''(2) \cdot A^5\, n_{1z}\, n_{2y}^2\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4d}$$

$$-\frac{3\varepsilon^4}{80\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f''(2) \cdot A^5\, n_{1y}\, n_{2y}\, n_{2z}\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4e}$$

$$\frac{\varepsilon^4}{2}\, \sigma_0^5 B_6^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f'(2) \cdot A^7\, n_{1y}\, n_{2y}\, \varDelta_x^4\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, V, \tag{4.4f}$$

$$\frac{3\varepsilon^4}{40\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f'(2) \cdot A^5\, n_{1y}\, n_{2y}\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4g}$$

$$\frac{\varepsilon^4}{80\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f'(1)\, f'(2) \cdot A^5\, n_{1z}\, n_{2z}\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4h}$$

$$\frac{\varepsilon^4}{80\pi}\, \sigma_0^5 B_4^*(T^*)\, \frac{\mathrm{d}^2}{16\pi^2} \int f''(1)\, f''(2) \cdot A^5\, n_{1y}^2\, n_{2y}^2\, \varDelta_x^2\, \mathrm{d}\varDelta\, \mathrm{d}\boldsymbol{n}_1\, \mathrm{d}\boldsymbol{n}_2\, VS, \tag{4.4i}$$

$$A = [1 + S_1 (\boldsymbol{n}_1 \cdot \varDelta)^2 + S_1 (\boldsymbol{n}_2 \cdot \varDelta)^2 - S_2 (\boldsymbol{n}_1 \cdot \varDelta)^2],$$
$$f(1, 2) = f(\cos\theta_{1,2}) \quad \text{where} \quad S = 4\pi R^2. \tag{4.5}$$

The integrals (4.4a), (4.4c) and (4.4f) are proportional to the volume of the sample, and the others are proportional to the product of V (volume) and S (surface). Those other terms look as if they are concerned with the coupling of the bulk and surface of the liquid crystal. The abovementioned coupling has never been derived from the microscopical point of view. Usually this feature was understood as the influence of the edge conditions, not as the coupling V–S.

5. Results and Discussion

The starting point of any particular investigation of a system with the spontaneously broken symmetry is the assumption of a model potential which leads to a negative value of K_2. After [1] we have chosen the following form of the potential energy:

$$U = 4\gamma\left(\left[\frac{\sigma}{r}\right]^m - \left[\frac{\sigma}{r}\right]^n\right) = U(\boldsymbol{r}, \boldsymbol{\Delta}, \boldsymbol{n}_1, \boldsymbol{n}_2). \quad (5.1)$$

This is the potential energy of two nonchiral uniaxial molecules whose centers are separated by a vector $\boldsymbol{r} = \boldsymbol{r}_2 - \boldsymbol{r}_1$ and whose long axes are parallel to the vectors $\boldsymbol{n}_1$ and $\boldsymbol{n}_2$. r is the length of $\boldsymbol{r}$, $\boldsymbol{\Delta}$ the unit vector pointing in the direction of $\boldsymbol{r}$ and m, n are the model parameters. This is the so-called Corner potential with Lennard-Jones type interaction. σ has the form suggested by Ruijgrok [1]:

$$\sigma = \sigma_0 + \sigma_1(\boldsymbol{\Delta} \cdot \boldsymbol{n}_1)^2 + \sigma_1(\boldsymbol{\Delta} \cdot \boldsymbol{n}_2)^2 - \sigma_2(\boldsymbol{n}_1 \cdot \boldsymbol{n}_2)^2, \quad (5.2)$$

where σ_0, σ_1, σ_2 are the fixed parameters with the dimension of length ($\sigma_1 = S_1\sigma_0$; $\sigma_2 = S_2\sigma_0$).

Particular values of the parameters which lead to a negative K_2 are

$$m = 12, \quad n = 6, \quad S_1 = -1.1, \quad S_2 = 0.00001.$$

K_1 and K_3 are positive, contrary to K_2. They are presented in Figure 2.

In Fig. 3 there is shown the equipotential surface due to the potential energy for these values of the parameters. We can compare it with the equipotential surface for a nematic with positive K_2 (Figure 4). Since these surfaces are connected with the shape of molecules, it is possible that sideports perpendicular to the long axes and placed in the middle of them are the reason of the spontaneously broken symmetry.

We would like to apply the abovementioned model potential in the expansion of the free energy of distortion due to twist.

We have to look back at (4.4). There are two types of integrals in (4.4): proportional to V and proportional to VS. We would like to ascertain if these integrals are of the same order. Since only B_i^* coefficients cast any doubts, we have to investigate their behaviour. We can calculate B_4^* and B_6^* from the expression

$$B_a^*(T^*) = \frac{1}{mi!}\left[\frac{4}{T^*}\right]^{\frac{a+1}{m}} \sum_{i=0}^{\infty} \Gamma\left[\frac{ni-(\alpha+1)}{m}\right]\left[\frac{4}{T^*}\right]^{\frac{(m-n)i}{m}}, \quad (5.3)$$

where m and n are parameters of the model potential.

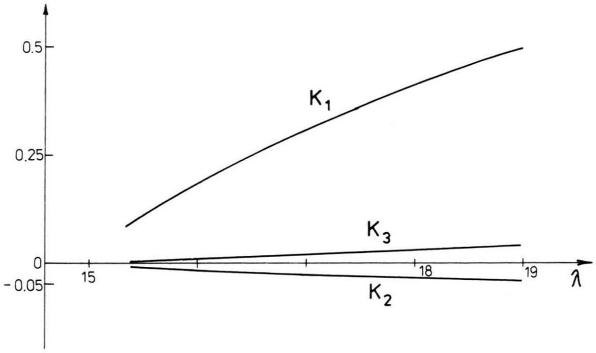

Fig. 2. Dimensionless elastic constants ($S_1 = -1.1$; $S_2 = 0.00001$).

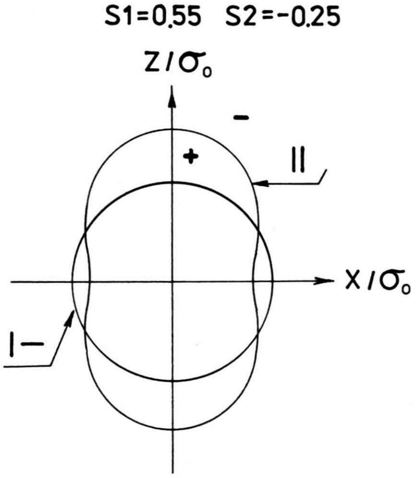

Fig. 3. Equipotential surface due to the potential energy for a nematic with negative K_2.

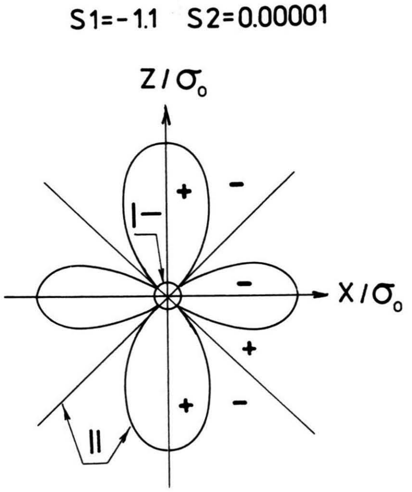

Fig. 4. Equipotential surface due to the potential energy for a nematic with positive K_2.

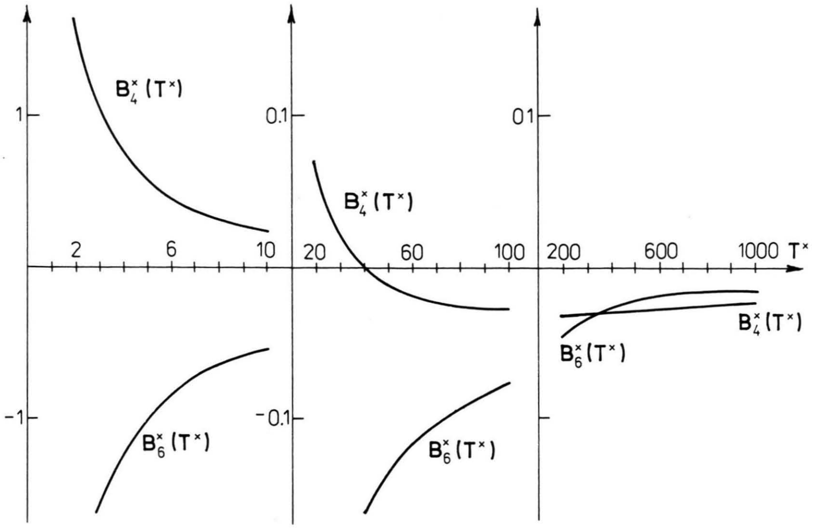

Fig. 5. Coefficients B_4^* and B_6^* as functions of the reduced temperature T^*.

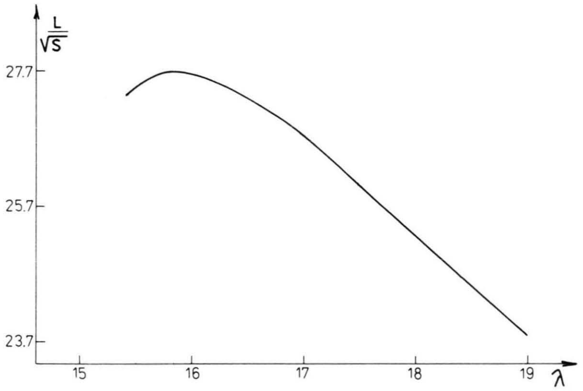

Fig. 6. Jump of the spontaneously twisted nematic devided by the square root of the surface S vs. the effective temperature λ.

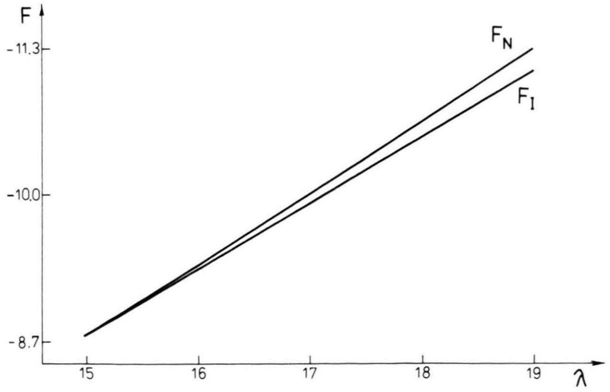

Fig. 7. Comparison of the energies for the nematic phase with spontaneously broken symmetry and the isotropic phase.

Table 1. Values of the F_2 (5.10), ψ (5.11) and $L/\sqrt{S}$ (5.8) calculated for the effective temperature λ corresponding to negative K_2.

λ	ψ	F_2	$L/\sqrt{S}$
19	381.013	−0.4288 e−1	23.784
18.5	376.39	−0.039	24.787
18	366.19	−0.0366	25.238
17.5	350.532	−0.033	26.004
17	326.05	−0.029	26.754
16	235.38	−0.0196	27.65
15.84	213.536	−0.0177	27.713
15.36	124.896	−0.0107	27.26

In Fig. 5 the behaviour of B_4^* and B_6^* is shown. One can see that B_4^* and B_6^* are of the same order. As the term σ_0^7 is much smaller than $\sigma_0^5 S$, we can neglect in (4.4) all integrals multiplied by B_6^*.

Expansion of F up to ε^4 reads

$$F = \tfrac{1}{2} K_2 V \varepsilon^2 + kT C_{VS} \varepsilon^4, \qquad (5.4)$$

where C_{VS} means the sum of all integrals from (4.4) which include products VS.

The necessary condition for the minimum of F leads to the equation for ε:

$$K_2 V \varepsilon + 4 \varepsilon^3 kT C_{VS} = 0. \qquad (5.5)$$

This equation has two solutions:

$$\varepsilon = 0, \qquad (5.6\text{a})$$

$$\varepsilon = \sqrt{\frac{-K_2 V}{4kT C_{VS}}}. \qquad (5.6\text{b})$$

Since the second derivative of F has the form

$$F'' = V K_2 + 12 \varepsilon^2 kT C_{VS}, \qquad (5.7)$$

Table 2. Nematic solutions (c_0, c_1, c_2, c_3) and values of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ calculated for the effective temperature λ corresponding to negative K_2.

λ	c_0	c_1	c_2	c_3	$\langle P_2 \rangle$	$\langle P_4 \rangle$
19	−3.602	5.965	−5.27e−4	−9.7e−8	0.709	0.358
18.5	−3.361	5.664	−4.83e−4	−4.0e−14	0.692	0.337
18	−3.111	5.347	−4.37e−4	−1.6e−14	0.671	0.313
17.5	−2.852	5.011	−3.9 e−4	−1.3e−14	0.647	0.288
17	−2.577	4.648	−3.41e−4	−1.1e−14	0.618	0.259
16	−1.943	3.764	−2.32e−4	−6.1e−15	0.531	0.187
15.84	−1.821	3.585	−2.11e−4	−5.4e−15	0.511	0.172
15.36	−1.341	2.84	−1.35e−4	−2.8e−15	0.417	0.113

the case $\varepsilon = 0$ corresponds to the maximum of F. The other one corresponds to the minimum.

We can write (5.6b) in the form

$$\frac{L_2}{\sqrt{S}} = \sqrt{\frac{\psi}{-5\pi F_2}}, \tag{5.8}$$

where we have used the expressions

$$K_2 = \frac{\pi}{32} kT d^2 \sigma_0^5 B_4^*(T^*) F_2(S_1, S_2), \tag{5.9}$$

$$F_2 = \frac{1}{\pi^3} \int \Delta_x^2 n_{1y} n_{2y} f'(\cos\theta_1) f'(\cos\theta_2) A^5 \,\mathrm{d}\boldsymbol{n}_1 \,\mathrm{d}\boldsymbol{n}_2 \,\mathrm{d}\Delta, \tag{5.10}$$

$$C_{VS} = VS(1/40)\,\sigma_0^5 B_4^*(T^*)\, d^2 (1/16)\,\pi^2 \psi, \tag{5.11}$$

$$\varepsilon = \pi/L_2, \quad \text{where } L_2 \text{ is the spiral jump.} \tag{5.12}$$

Equation (5.8) describes the spiral jump in the spontaneously twisted nonchiral nematic. Table 1 presents the values of F_2, ψ, $L/\sqrt{S}$ calculated for the values of the model parameters which lead to the negative value of K_2. Figure 6 shows the dependence of the L_2 spiral jump upon the λ effective temperature. One can see that these values of the jump are comparable with the values of $\sqrt{S}$, therefore the spontaneous twist might be unnoticeable.

The last problem we will discuss is the phase transition from the isotopic to the nematic phase vs. an effective temperature. The single particle distribution function which has been used in all calculations has the form [1]

$$f(x) = \exp(c_0 + c_1 x^2 + c_2 x^4 + c_3 x^6), \tag{5.13}$$

where c_0, c_1, c_2, and c_3 are the coefficients depending on the effective temperature λ:

$$\lambda = -(\pi/6)\,\sigma_0^3 B_2^*(T^*)\, d\,. \tag{5.14}$$

Values of c_i corresponding to the chosen microscopic parameters are listed in Table 2. These nematic solutions (c_0, c_1, c_2, c_3) are stable when the total free energy of the nematic phase is smaller than the free energy of an isotropic phase ($c_0 = c_1 = c_2 = c_3 = 0$). Since $\varepsilon^2 \sim 10^{-27}$, the value of the distortion free energy is much smaller than the free energy of the untwisted nematic. Therefore we can compare only energies for the isotropic and undistorted nematic phases. These energies are shown in Figure 7. One can easily see that the nematic phase satisfies the stability condition. The crossing point of these free energies corresponds to the critical value of λ_c due to the phase transition from the isotropic to the twisted nematic phase. From this figure we find $\lambda_c = 15.416$. Since the order parameters

$$\langle P_n \rangle = \int_0^1 P_n(x) f(x)\,\mathrm{d}x \tag{5.15}$$

show a discontinuity at this point, the temperature T_c corresponding to λ_c is identical with the experimental value of the critical temperature.

Experimental evidence of the existence of the twisted nematic phase can be obtained by the investigation of the Freederiks effect. For negative K_2 this phenomenon should appear as a continuous transition vs. magnetic field.

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